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IChO

International Chemistry Olympiad

6 theoretical problems
2 practical problems

THE THIRTY-FIRST
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THEORETICAL PROBLEMS

PROBLEM 1

A compound **Q** (molar mass 122.0 g mol^{-1}) consists of carbon, hydrogen and oxygen.

PART A

The standard enthalpy of formation of CO_2(g) and H_2O(l) at 25.00 ℃ are –393.51 and –285.83 kJ mol^{-1}, respectively. The gas constant, R = 8.314 J K^{-1} mol^{-1}.
(Relative atomic masses : H = 1.0; C = 12.0; O = 16.0)

A sample of solid **Q** that weighs 0.6000 g, is combusted in an excess of oxygen in a bomb calorimeter, which initially contains 710.0 g of water at 25.000 ℃. After the reaction is completed, the temperature is observed to be 27.250 ℃, and 1.5144 g of CO_2 (g) and 0.2656 g of H_2O(l) are produced.

1.1 Determine the molecular formula and write a balanced equation with correct state of matters for the combustion of **Q**.

If the specific heat of water is 4.184 J g^{-1} K^{-1} and the internal energy change of the reaction (ΔU^0) –3079 kJ mol^{-1}.

1.2 Calculate the heat capacity of the calorimeter (excluding the water).

1.3 Calculate the standard enthalpy of formation ($\Delta H_f{}^0$) of **Q**.

PART B

The following data refer to the distribution of **Q** between benzene and water at 6 ℃, C_B and C_W being equilibrium concentrations of the species of **Q** in the benzene and water layers, respectively:

Assume that there is only one species of **Q** in benzene independent of concentration and temperature.

Concentration (mol dm^{-3})	
C_B	C_W
0.0118	0.00281
0.0478	0.00566
0.0981	0.00812
0.156	0.0102

1.4 Show by calculation whether **Q** is monomer or dimer in benzene. Assume that **Q** is a monomer in water.

The freezing point depression, for an ideal dilute solution, is given by

$$T_f^0 - T_f = \frac{R(T_f^0)^2 \, X_s}{\Delta H_f}$$

where T_f is the freezing point of the solution, T_f^0 the freezing point of solvent, ΔH_f the heat of fusion of the solvent, and X_s the mole fraction of solute. The molar mass of benzene is 78.0 g mol^{-1}. At 1 atm pure benzene freezes at 5.40 ℃. The heat of fusion of benzene is 9.89 kJ mol^{-1}.

1.5 Calculate the freezing point (T_f) of a solution containing 0.244 g of **Q** in 5.85 g of benzene at 1 atm.

SOLUTION

PART A

1.1 Mole C : H : O = $\frac{\frac{15144 \times 12.0}{44.0}}{12.0} : \frac{\frac{0.2656 \times 2.0}{18.0}}{1.0} : \frac{0.1575}{16.0}$

= 0.0344 : 0.0295 : 0.00984 = 7 : 6 : 2

The formula mass of $C_7H_6O_2$ = 122 which is the same as the molar mass given.

$C_7H_6O_2(s) + 15/2\ O_2(g) \rightarrow 7\ CO_2(g) + 3\ H_2O(l)$ or

$2\ C_7H_6O_2(s) + 15\ O_2(g) \rightarrow 14\ CO_2(g) + 6\ H_2O(l)$

1.2 $n(\mathrm{Q}) = \dfrac{0.6000}{122.0} = 4.919\times10^{-3}$ mol

$q_v = n\,\Delta U^0 = \dfrac{0.6000}{122.0} \times (-3079) = -15.14$ kJ

Total heat capacity = $\dfrac{-q_v}{\Delta T} = \dfrac{15.14}{2.250} = 6.730$ kJ K^{-1}

Heat capacity of water = $710.0 \times 4.184 = 2971$ J K^{-1}

Heat capacity of calorimeter = $6730 - 2971 = 3759$ J K^{-1}

1.3 $\Delta n_g = 7 - 15/2 = -0.5$ mol

$\Delta H° = \Delta U° + RT\,\Delta n_g = -3079 + (8.314\times10^{-3}) \times (298) \times (-0.5) = -3079 - 1 = -3080$

$\Delta H° = (7\,\Delta_f H°, CO_2(g) + 3\,\Delta_f H°, H_2O(l)) - (\Delta_f H°, Q)$

$\Delta_f H°$ of Q = $7 \times (-393.51) + 3 \times (-285.83) - (-3080) = -532$ kJ mol^{-1}

PART B

1.4

c_B (mol dm^{-3})	0.0118	0.0478	0.0981	0.156
c_W (mol dm^{-3})	0.00281	0.00566	0.00812	0.0102
either c_B/c_W	4.20	8.44	12.1	15.3
or c_B/c_w^2	1.49×10^3	1.49×10^3	1.49×10^3	1.50×10^3
(or $\sqrt{c_B}\,/\,c_W$	38.6	38.6	38.6	38.7)

From the results show that the ratio c_B/c_W varies considerably, whereas the ratio c_B/c_w^2 or $\sqrt{c_B}\,/\,c_W$ is almost constant, showing that in benzene, Q is associated into double molecule. Q in benzene is dimer.

1.5 If Q is completely dimerized in benzene, the apparent molecular mass should be 244.

Mole fraction of $Q_2 = \dfrac{\dfrac{0.244}{244}}{\dfrac{0.244}{244} + \dfrac{5.85}{78.0}} = 1.32\times10^{-2}$ (0.01316)

$\Delta T_f = \dfrac{8.314 \times 278.55^2}{9.89\times10^3} \times 1.32\times10^{-2} = 0.861$

$T_f = 5.40 - 0.861 = 4.54$ ℃

PROBLEM 2

PART A

A diprotic acid , H_2A , undergoes the following dissociation reactions :

$$H_2A \rightleftharpoons HA^- + H^+; \qquad K_1 = 4.50\times10^{-7}$$

$$HA^- \rightleftharpoons A^{2-} + H^+; \qquad K_2 = 4.70\times10^{-11}$$

A 20.00 cm^3 aliquot of a solution containing a mixture of Na_2A and NaHA is titrated with 0.300 M hydrochloric acid. The progress of the titration is followed with a glass electrode *pH* meter. Two points on the titration curve are as follows :

cm^3 HCl added	*pH*
1.00	10.33
10.00	8.34

2.1 On adding 1.00 cm^3 of HCl, which species reacts first and what would be the product?

2.2 What is the amount (mmol) of the product formed in (2.1)?

2.3 Write down the main equilibrium of the product from (2.1) reacting with the solvent?

2.4 What are the amounts (mmol) of Na_2A and NaHA initially present?

2.5 Calculate the total volume of HCl required to reach the second equivalence point.

PART B

Solutions I, II and III contain a *pH* indicator HIn ($K_{In} = 4.19\times10^{-4}$) and other reagents as indicated in the table. The absorbance values at 400 nm of the solutions measured in the same cell, are also given in the table. K_a of CH_3COOH is 1.75×10^{-5}.

Table:

	Solution I	Solution II	Solution III
Total concentration of indicator HIn	1.00×10^{-5} M	1.00×10^{-5} M	1.00×10^{-5} M
Other reagents	1.00 M HCl	0.100 M NaOH	1.00 M CH_3COOH
Absorbance at 400	0.000	0.300	?

2.6 Calculate the absorbance at 400 nm of solution III.

2.7 Apart from H_2O, H^+ and OH^-, what are all the chemical species present in the solution resulting from mixing solution II and solution III at 1 : 1 volume ratio?

2.8 What is the absorbance at 400 nm of the solution in (2.7)?

2.9 What is the transmittance at 400 nm of the solution in (2.7)?

SOLUTION

PART A

2.1 Species which reacts first is A^{2-}.

The product is HA^-.

2.2 n(product) = 1.00×0.300 = 0.300 mmol

2.3 $HA^- + H_2O \rightleftharpoons H_2A + OH^-$

2.4 At *pH* 8.34 which is equal to $(pK_{a1} + pK_{a2}) / 2$ all A^- are protonated as HA^-.

Therefore $n(A^{2-})$ initially present in the solution = 0.300×10.00 = 3.00 mmol

At *pH* = 10.33, the system is a buffer in which the ratio of $[A^{2-}]$ and $[HA^-]$ is equal to 1.

Thus

$[HA^-]_{initial} + [HA^-]_{formed} = [A^{2-}]_{jnitial} - [HA^-]_{formed}$

$n(HA^-)_{initial}$ = 3.00 – 0.300 – 0.300 mmol = 2.40 mmol

$n(Na_2A)$ = <u>3.00 mmol</u>

n(NaHA) = <u>2.40 mmol</u>

2.5 Total volume of HCl required = $[(2 \times 3.00) + 2.40] / 0.300$ = 28.00 cm^3

PART B

2.6 Solution III is the indicator solution at 1×10^{-5} M in a solution containing 1.0 M CH_3COOH.

To obtain the absorbance of the solution, it is necessary to calculate the concentration of the basic form of the indicator which is dependent on the $[H^+]$ of the solution.

$[H^+]$ of solution III = $\sqrt{K_a c} = \sqrt{1.75\times10^{-5}\times1.0} = 4.18\times10^{-3}$

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

$$\frac{[In^-]}{[HIn]} = \frac{K_{In}}{[H^+]} = \frac{1\times10^{-3.38}}{1\times10^{-2.38}} = 0.100$$

Since $[HIn] + [In^-] = 1\times10^{-5}$

$10\,[In^-] + [In^-] = 1\times10^{-5}$

$[In^-] = 0.091\times10^{-5}$

Absorbance of solution III = $\frac{0.091\times10^{-5}}{1.00\times10^{-5}}\times 0.300 = 0.027$

2.7 All the chemical species present in the solution resulting from mixing solution II and solution III at 1 : 1 volume ratio (apart from H^+, OH^- and H_2O) are the following: CH_3COOH , CH_3COO^-, Na^+ , HIn , In^-.

2.8 When solutions II and III are mixed at 1 : 1 volume ratio, a buffer solution of 0.05 M CH_3COO^- / 0.45 M CH_3COOH is obtained.

$[H^+]$ of the mixture solution = $K_a \frac{[CH_3COOH]}{[CH_3COO^-]} = 1.75\times10^{-5}\times\frac{0.45}{0.05} = 15.75\times10^{-5}$

$$\frac{[In^-]}{[HIn]} = \frac{K_{In}}{[H^+]} = \frac{1\times10^{-3.38}}{15.75\times10^{-5}} = 2.65$$

Since $[HIn] + [In^-] = 1\times10^{-5}$

$\frac{[In^-]}{2.65} + [In^-] = 1\times10^{-5}$

$[In^-] = 0.726\times10^{-5}$

Absorbance of solution = $\frac{0.726\times10^{-5}}{1.00\times10^{-5}}\times 0.300 = 0.218$

2-9 Transmittance of solution = $10^{-0.218} = 0.605 \Rightarrow 60.5\%$

PROBLEM 3

One of naturally occurring radioactive decay series begins with $^{232}_{90}Th$ and ends with a stable $^{208}_{82}Pb$.

3.1 How many beta (β^-) decays are there in this series? Show by calculation.

3.2 How much energy in MeV is released in the complete chain?

3.3 Calculate the rate of production of energy (power) in watts (1 W = J s^{-1}) produced by 1.00 kilogram of ^{232}Th ($t_{½} = 1.40\times10^{10}$ years).

3.4 ^{228}Th is a member of the thorium series. What volume in cm^3 of helium at 0 °C and 1 atm collected when 1.00 gram of ^{228}Th ($t_{1/2}$ = 1.91 years) is stored in a container for 20.0 years. The half-lives of all intermediate nuclides are short compared to the half-life of ^{228}Th.

3.5 One member of thorium series, after isolation, is found to contain 1.50×10^{10} atoms of the nuclide and decays at the rate of 3440 disintegrations per minute. What is the half-life in years?

The necessary atomic masses are :

$^{4}_{2}He$ = 4.00260 u, $^{208}_{82}Pb$ = 207.97664 u, $^{232}_{90}Th$ = 232.03805 u; and 1u = 931.5 MeV

1 MeV = 1.602×10^{-13} J

$N_A = 6.022\times10^{23}$ mol^{-1}

The molar volume of an ideal gas at 0 °C and 1 atm is 22.4 dm^3 mol^{-1}.

SOLUTION

3.1 A = 232 – 208 = 24; 24/4 = 6 alpha particles

The nuclear charge is therefore reduced by $2 \times 6 = 12$ units, however, the difference in nuclear charges is only 90 – 82 = 8 units. Therefore there must be

12 – 8 = 4 β^- emitted.

Number of beta decays = 4

3.2 $^{232}_{90}Th \rightarrow {}^{208}_{82}Pb + 6\,{}^{4}_{2}He + 4\beta^-$

Energy released is Q value

$Q = [m(^{232}\text{Th}) - m(^{208}\text{Pb}) - 6\,m(^{4}\text{He})]\,c^2$

(the mass of $4e^-$ are included in daughters)

$= [232.03805\,u - 207.97664\,u - 6 \times 4.00260\,u] \times 931.5\ \text{MeV u}^{-1} =$

$= (0.04581u) \times (931.5\ \text{MeV}) = 42.67\ \text{MeV}$

3.3 The rate of production of energy (power) in watts (1 W = J s^{-1}) produced by 1.00 kilogram of ^{232}Th ($t_{1/2} = 1.40\times10^{10}$ years).

1.00 kg contains = $\dfrac{1000\ \text{g} \times 6.022\times10^{23}\ \text{mol}^{-1}}{232\ \text{g mol}^{-1}} = 2.60\times10^{24}$ atoms

Decay constant for ^{232}Th:

$$\lambda = \frac{0.693}{1.40\times10^{10}\ \text{y} \times 3.154\times10^{7}\ \text{s y}^{-1}} = 1.57\times10^{-18}\ \text{s}^{-1}$$

For activity: $A = N\,\lambda = 2.60\times10^{24} \times 1.57\times10^{-18} = 4.08\times10^{6}$ dis s^{-1}

(disintegrations s^{-1})

Each decay liberates 42.67 MeV

Rate of production of energy (power):

4.08×10^{6} dis $s^{-1} \times 42.67$ MeV $dis^{-1} \times 1.602\times10^{-13}$ J MeV^{-1} =

$= 2.79\times10^{-5}$ J $s^{-1} = 2.79\times10^{-5}$ W

3.4 The volume in cm^3 of helium at 0 ℃ and 1 atm collected when 1.00 gram of ^{228}Th ($t_{1/2}$ = 1.91 years) is stored in a container for 20.0 years.

$^{228}\text{Th} \rightarrow {}^{208}\text{Pb} + 5\ {}^{4}\text{He}$

The half-lives of various intermediates are relatively short compared with that of ^{228}Th.

$$A = \lambda N = \frac{0.693}{1.91\,\text{y}} \times \frac{1.000\ \text{g} \times 6.022\times10^{23}\ \text{mol}^{-1}}{228\ \text{g mol}^{-1}} = 9.58\times10^{20}\ \text{y}^{-1}$$

Number of He collected:

$N_{He} = 9.58\times10^{20}\ \text{y}^{-1} \times 20.0\ \text{y} \times 5$ particles $= 9.58\times10^{22}$ particles of He

$$V_{He} = \frac{9.58\times10^{22} \times 22{,}4\ \text{dm}^3\,\text{mol}^{-1}}{6.022\times10^{23}\ \text{mol}^{-1}} = 3.56\ \text{dm}^3 = 3.56\times10^{3}\ \text{cm}^3$$

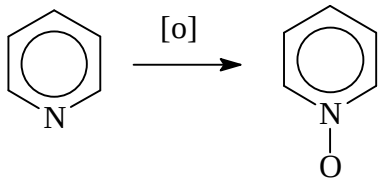
3.5 The half-life:

$A = \lambda N$

$$t_{½} = \frac{0.693}{\lambda} = \frac{0.693\,N}{A} = \frac{0.693 \times 510 \times 10^{10}\ \text{atoms}}{3440\ \text{atoms min}^{-1}} = 3.02 \times 10^{6}\ \text{min} = 5.75\ \text{years}$$

PROBLEM 4

Ligand **L** can form complexes with many transition metals. **L** is synthesized by heating a mixture of a bipyridine, glacial acetic acid and hydrogen peroxide to 70 – 80 °C for 3 hrs. The final product **L** crystallizes out as fine needles and its molecular mass is 188. An analogous reaction with pyridine is ;



Complexes of **L** with Fe and Cr have the formulae of $FeL_m(ClO_4)_n$. 3 H_2O (**A**) and $CrL_xCl_y(ClO_4)_z.H_2O$ (**B**), respectively. Their elemental analyses and physical properties are given in Tables 4a and 4b. The relationship of colour and wavelength is given in Table 4c.

Table 4a: Elemental analyses.

Complex	Elemental analyses , (wt. %)
A	Fe 5.740, C 37.030, H 3.090 , Cl 10.940, N 8.640
B	Cr 8.440, C 38.930, H 2.920, Cl 17.250, N 9.080

Use the following data:

Atomic number: Cr = 24, Fe = 26

Relative atomic mass: H = 1, C = 12, N = 14, O = 16, Cl = 35.45, Cr = 52, Fe = 55.8

Table 4b: Physical properties

Complex	Magnetic moment , μ B.M.	Colour
A	6.13	Yellow
B	Not measured	Purple

Table 4c Relationship of wavelength to colour.

Wavelength (nm) and colour absorbed	Complementary colour
400 (violet)	Yellow Green
450 (blue)	Yellow
490 (blue green)	Orange
500 (green)	Red
570 (yellow green)	Violet
580 (yellow)	Blue
600 (orange)	Blue green
650 (red)	Green

4.1 Write down the molecular formula of **L**.

4.2 If **L** is a bidentate chelating ligand, draw the structure of the bipyridine used. Also draw the structure of **L** .

4.3 Does the ligand **L** have any charge, i. e. net charge?

4.4 Draw the structure when one molecule of **L** binds to metal ion (M).

4.5 From the data in Table 4a, determine the empirical formula of **A**. What are the values of m and n in $FeL_m(ClO_4)_n$ .3 H_2O? Write the complete formula of **A** in the usual IUPAC notation. What is the ratio of cation to anion when **A** dissolves in water?

4.6 What is the oxidation number of Fe in **A**? How many d-electrons are present in Fe ion in the complex? Write the high spin and the low spin configurations that may exist for this complex. Which configuration, high or low spin, is the correct one? What is the best evidence to support your answer?

4.7 From Table 4c, estimate λ_{max} (nm) of **A**.

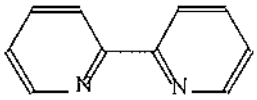
4.8 Detail analysis of **B** shows that it contains Cr^{3+} ion. Calculate the 'spin-only' magnetic moment of this compound.

4.9 Compound **B** is a 1 : 1 type electrolyte. Determine the empirical formula of **B** and the values of x, y, z in $CrL_xCl_y(ClO_4)_z$. H_2O.

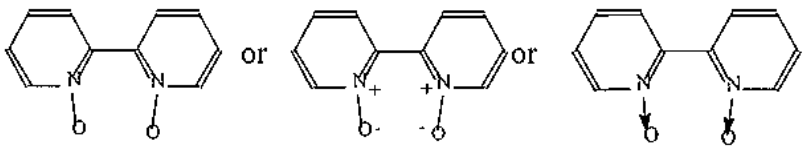
SOLUTION

4.1 Knowing that L was synthesized from bipyridine and during the reaction bipyridine was simply oxidized to bipyridine oxide. The molecular mass of bipyridine is 156 (for $C_{10}H_8N_2$) while the molecular mass of **L** is 188. The difference of 32 is due to 2 atoms of oxygen. Therefore, the molecular formula of **L** is $C_{10}H_8N_2O_2$.

4.2 The structures of bipyridine and **L**:



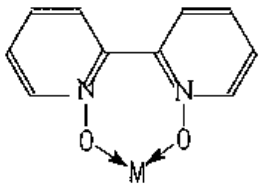
Structure of bipyridine



structure of **L**

4.3 The ligand **L** has no charge.

4.4 The structure when one molecule of **L** binds to metal ion (M):



4.5 The empirical formula of **A**. Calculation:

	Fe	C	H	Cl	N	O
%	5.740	37.030	3.090	10.940	8.640	34.560*
mol	0.103	3.085	3.090	0.309	0.617	2.160
mol ratio	1.000	29.959	30.00	2.996	5.992	20.971
atom ratio	1	30	30	3	6	21

*) Percentage of O is obtained by difference.)

The empirical formula of **A** is $FeC_{30}H_{30}Cl_3N_6C_{21}$

The values of m and n in $FeL_m(C104)_n$. 3 H_2O:

Since the molecular formula contains one atom of Fe, so in this case the empirical formula is equivalent to the molecular formula. The molecular formula of **L** has been

obtained previously in (4a) and (4b), therefore we can work to find m = 3. Having obtained the value of m , one can work out for n and find that n = 3.

The complete formula of **A** is $[FeL_3](ClO_4)_3 \cdot 3\ H_2O$

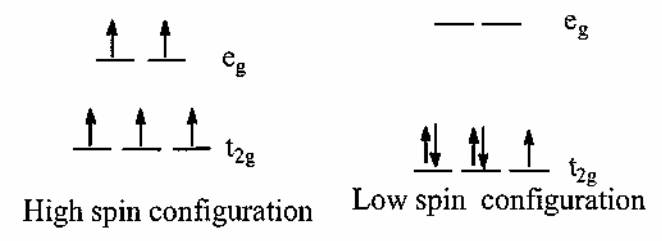
The ratio of cation to anion is equal to 1 : 3.

The three ClO_4^- groups will dissociate as free ion in solution. So the entire complex will be in the ion forms as $[FeL_3]^{3+}$ and 3 ClO_4^- in solution.

4.6 The oxidation number of Fe in complex **A** is +3 or III.

The number of *d*-electrons in Fe^{3+} ion in the complex = 5.

The high spin and the low spin configuration that may exist for this complex:



The correct answer is high spin configuration.

The best evidence to support your answer for this high/low spin selection is magnetic moment.

There exist a simple relation between number of unpaired electrons and the magnetic moment as follows:

$$\mu = \sqrt{n(n+2)}$$

where μ is the so-called 'spin-only' magnetic moment and n is the number of unpaired electrons. Thus, for high spin configuration in the given case,

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92\ \text{B.M.}$$

For low spin case:

$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73\ \text{B.M.}$$

The measured magnetic moment, for **A** is 6.13 B.M. (Table 4b) which is in the range for high spin configuration. Therefore, we can conclude that **A** can exist as a high spin complex.

4.7 From Table 4c, the color absorbed is complementary to the color seen. Thus, λ_{max} for complex A is 450 nm.

4.8 The 'spin-only' magnetic moment of complex **B**.

For Cr^{3+}: n = 3

Therefore, $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ B.M.

4.9 The empirical formula of B is $Cr_{20}H_{18}N_4Cl_3O_9$, i.e. x = 2, y = 2, z = 1.

PROBLEM 5

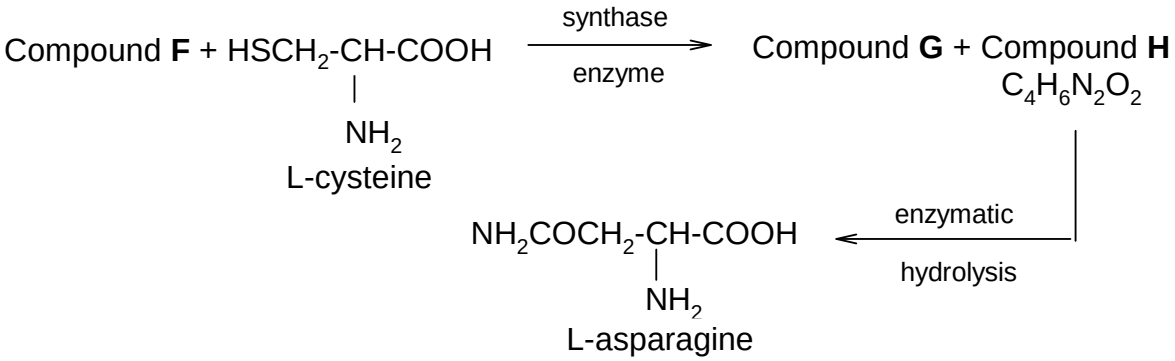
Glycoside **A** ($C_{20}H_{27}NO_{11}$), found in seeds of *Rosaceae* gives a negative test with Benedicts' or Fehling's solutions. Enzymatic hydrolysis of **A** yields (-) **B**, C_8H_7NO and **C**, $C_{12}H_{22}O_{11}$, but complete acid hydrolysis gives as organic products, (+) **D**, $C_6H_{12}O_6$ and (-) **E**, $C_8H_8O_3$.

C has a β-glycosidic linkage and gives positive test with Benedicts' or Fehling's solution. Methylation of **C** with MeI/Ag_2O gives $C_{20}H_{38}O_{11}$, which upon acidic hydrolysis gives 2,3,4-tri-*O*-methyl-D-glucopyranose and 2,3,4,6-tetra-*O*-methyl-D-glucopyranose.

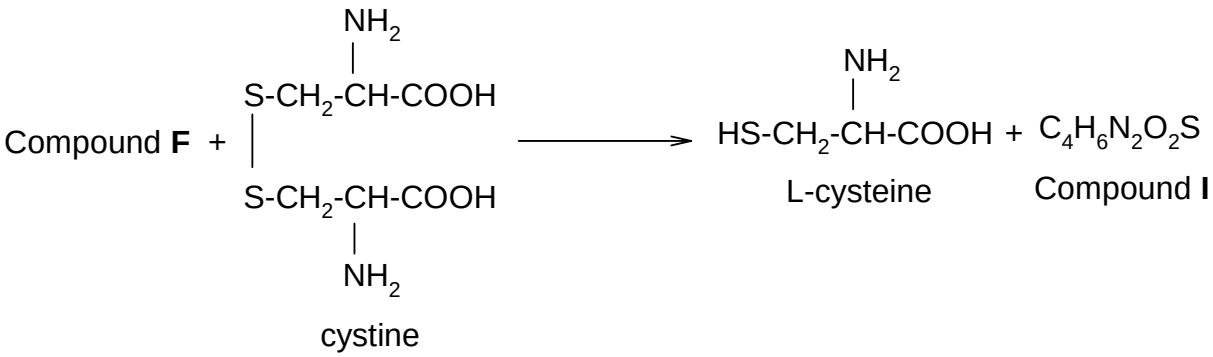
(±)**B** can be prepared from benzaldehyde and $NaHSO_3$ followed by NaCN. Acidic hydrolysis of (±)**B** gives (±)**E**, $C_8H_8O_3$.

5.1 Write structures of **A** – **D** with appropriate stereochemistry in Haworth projection, except for **B**.

Glycoside **A** is found to be toxic and believed to be due to extremely toxic compound **F**, liberated under the hydrolytic conditions. Detoxification of compound **F** in plant may be accompanied by the reactions (stereochemistry not shown).



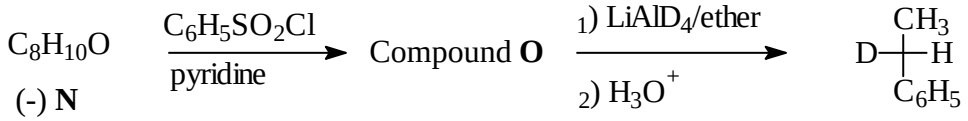
A small amount of compound **F** in human being is believed to be detoxified by a direct reaction with cystine giving L-cysteine and compound **I**, $C_4H_6N_2O_2S$ which is excreted in urine (stereochemistry not shown).



Compound **I** shows no absorption at 2150-2250 cm^{-1} in its IR spectrum but a band at 1640 cm^{-1} and the bands of carboxyl group are observed.

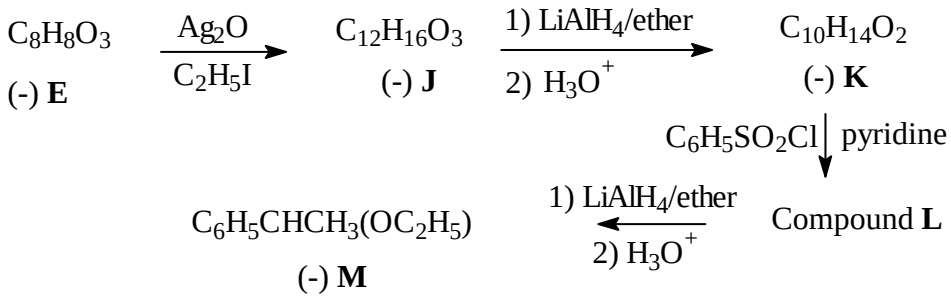
5.2 Write molecular formula for compounds **F** and **G,** and structural formula for compounds **H** and **I** and indicate stereochemistry of **H**. (Table 5.1 may be useful for structure identification.)

(-)1-Phenylethane-1-*d*, $C_6H_5CHDCH_3$ can be prepared in optically active form and the magnitude of its rotation has the relatively high value, $[\alpha]_D$ is equal to -0.6.

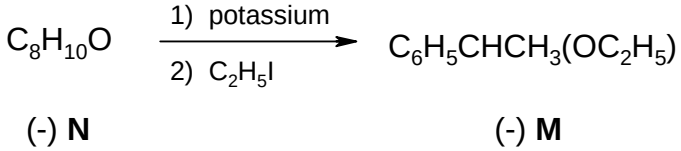


(-) 1-phenylethane-1-*d*

The absolute configuration of (-)1-phenylethane-1-*d* is related to (-) **E** according to the following reactions.



Compound (-) **M** can also be obtained from compound **N** as follows.



5.3 Deduce the absolute configuration of (-) **E** and the structure with configuration of each intermediate (**J – O**) in the sequence with the proper *R*,*S*-assignment as indicated in the answer sheet.

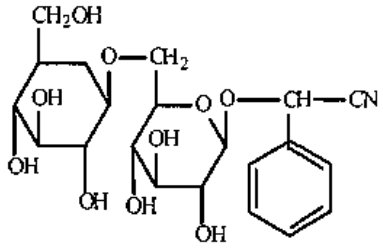
5.4 Choose the mechanism involved in the conversion of compound **O** to 1-phenylethane-*1-d*.

Table 5.1 Characteristic Infrared Absorption

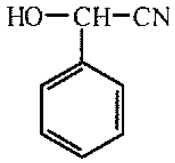
Stretching Vibration	Region (cm^{-1})	Stretching Vibration	Region (cm^{-1})
C-H (alkane)	2850-2960	O-H (free alcohol)	3400-3600
C-H (alkene)	3020-3100	O-H (H-bonded alcohol)	3300-3500
C=C	1650-1670	O-H (acid)	2500-3100
C-H (alkyne)	3300	C-O	1030-1150
C≡C	2100-2260	NH, NH_2	3310-3550
C-H (aromatics)	3030	C-N	1030, 1230
C=C (aromatics)	1500-1600	C=N	1600-1700
C-H (aldehyde)	2700-2775, 2820-2900	C≡N	2210-2260
C=O	1670-1780		

SOLUTION

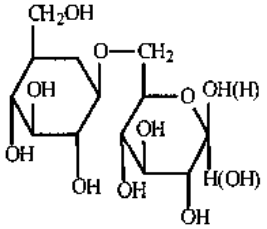
5.1



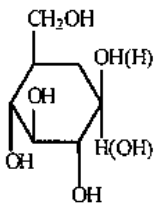
A



B



C

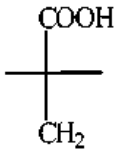


D

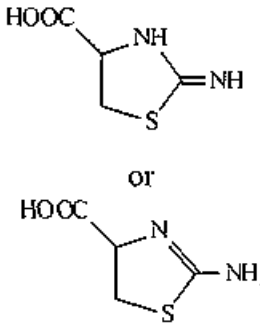
5.2

Molecular formula of compound **F** = HCN

Molecular formula of compound **G** = H_2S

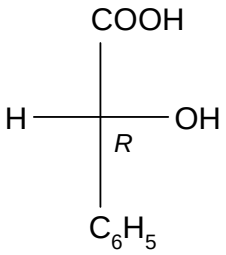


Compound **H**

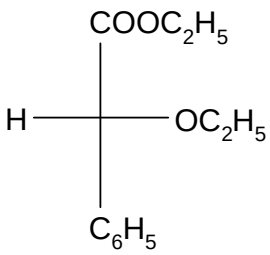


Compound **I**

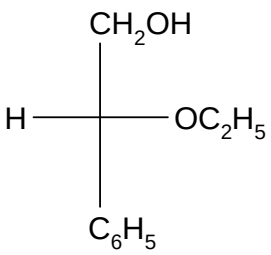
5.3



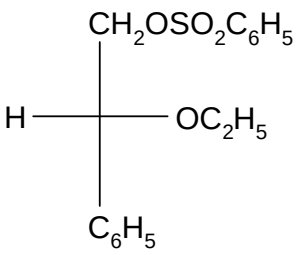
(-) **E**



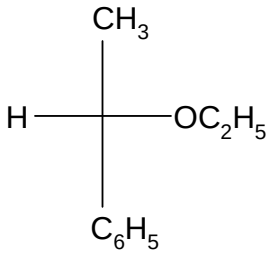
(-) **J**



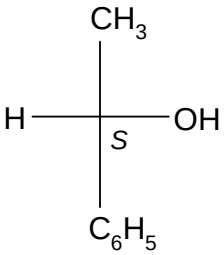
(-) **K**



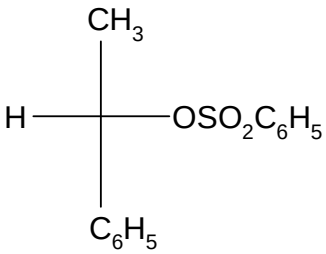
Compound **L**



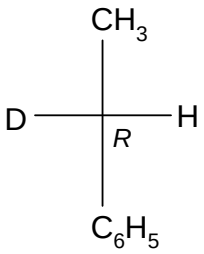
(-) **M**



(-) **N**



Compound **O**



(-) 1-phenylethane-*1-d*

5.4 The mechanism involved in the conversion of compound **O** to (-) 1-phenylethane-*1-d* is S_N2.

PROBLEM 6

Peptide **A** has a molecular weight of 1007. Complete acid hydrolysis gives the following amino acids in equimolar amounts: Asp, Cystine, Glu, Gly, Ile, Leu, Pro, and Tyr (see Table 1). Oxidation of **A** with HCO_2OH gives only **B** which carries two residues of cysteic acid (**Cya** which is a cysteine derivative with its thiol group oxidized to sulfonic acid).

6.1 How many sulphonic acid groups are formed from oxidation of a disulfide bond ?

Partial hydrolysis of **B** gives a number of di and tri-peptides (B1-B6). The sequence of each hydrolysis product is determined in the following ways.

The N-terminal amino acid is identified by treating the peptide with 2,4-dinitrofluorobenzene (DNFB) to give DNP-peptide. After complete acid hydrolysis of the DNP-peptide, a DNP-amino acid is obtained which can be identified readily by comparison with standard DNP-amino acids.

6.2 B1, on treatment with DNFB followed by acid hydrolysis gives a product, DNP-Asp. This suggests that B1 has aspartic acid at the N-terminus. Write down the <u>complete</u> structure of DNP-Asp at its isoelectric point (no stereochemistry required).

Next, the C-terminal amino acid is identified by heating the peptide at 100 °C with hydrazine, which cleave all the peptide bonds and convert all except C-terminal amino acids into amino acid hydrazides, leaving the C-terminal carboxyl group intact.

In this way N- and C-terminal amino acids are identified and the complete sequences of B1-B6 are as shown :

B1	Asp-Cya	B4	Ile-Glu
B2	Cya-Tyr	B5	Cya-Pro-Leu
B3	Leu-Gly	B6	Tyr-Ile-Glu

Hydrolysis of **B** with an enzyme from *Bacillus subtilis* gives B7-B9 with the following compositions:

B7 Gly-NH_2 (Glycinamide)

B8 Cya, Glu, Ile, Tyr

B9 Asp, Cya, Leu, Pro

6.3 Write down the sequence of B8, if DNP-Cya is obtained on treatment of B8 with DNFB followed by complete acid hydrolysis.

6.4 If the N- and C-terminal amino acids of B9 are identified as Asp and Leu respectively, write down the sequence of B9.

6.5 Write down the complete structure of **A** using abbreviation in Table 1, indicating the position of the disulfide bond.

However, the calculated molecular weight of **A** based on the above sequence is 2 mass units higher than the experimental value. On careful observation of the mixture from complete acid hydrolysis of **A**, 3 molar equivalents of ammonia are also produced in addition to the amino acids detected initially.

6.6 Suggest the revised structure of **A** and circle the site(s) of the structure to indicate all the possible source of ammonia.

6.7 Using the information in Table 2, calculate the isoelectric point of **A**.

Table 1**:** Formulae and symbols of common amino acids at isoelectric point

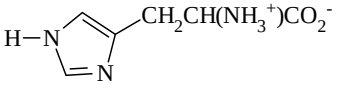
Name	Formula	Three-letter symbol
Alanine	$CH_3CH(NH_3^+)CO_2^-$	Ala
Arginine	$H_2NC(=NH)NH(CH_2)_3CH(NH_3^+)CO_2^-$	Arg
Asparagine	$H_2NCOCH_2CH(NH_3^+)CO_2^-$	Asn
Aspartic Acid	$HO_2CCH_2CH(NH_3^+)CO_2^-$	Asp
Cysteine	$HSCH_2CH(NH_3^+)CO_2^-$	Cys
Cystine	$[SCH_2CH(NH_3^+)CO_2^-]_2$	-
Glutamic Acid	$HO_2CCH_2CH_2CH(NH_3^+)CO_2^-$	Glu
Glutamine	$H_2NCOCH_2CH_2CH(NH_3^+)CO_2^-$	Gln
Glycine	$^+H_3NCH_2CO_2^-$	Gly
Histidine		His
Isoleucine	$CH_3CH_2CH(CH_3)CH(NH_3^+)CO_2^-$	Ile
Leucine	$(CH_3)_2CHCH_2CH(NH_3^+)CO_2^-$	Leu
Lysine	$H_2N(CH_2)_4CH(NH_3^+)CO_2^-$	Lys

Table 1 (continued)

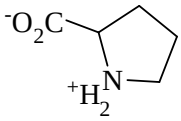
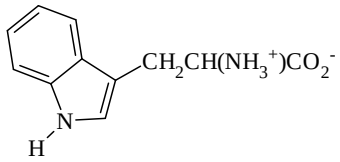
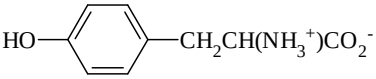
Methionine	$CH_3SCH_2CH_2CH(NH_3^+)CO_2^-$	Met
Phenylalanine	$PhCH_2CH(NH_3^+)CO_2^-$	Phe
Proline		Pro
Serine	$HOCH_2CH(NH_3^+)CO_2^-$	Ser
Threonine	$CH_3CH(OH)CH(NH_3^+)CO_2^-$	Thr
Tryptophan		Trp
Tyrosine		Tyr
Valine	$(CH_3)_2CHCH(NH_3^+)CO_2^-$	Val

Table 2: pK_a of some important groups in amino acids

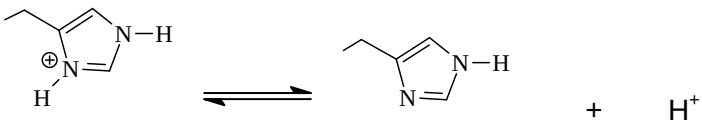
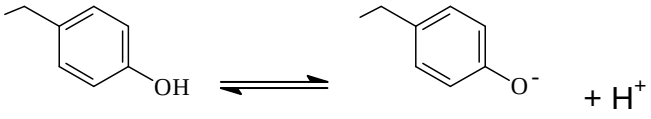
Groups	**Equilibrium**	**pK_a**
Terminal carboxyl	$-CO_2H \rightleftharpoons -CO_2^- + H^+$	3.1
Asp /or Glu side- chain carboxyl	$-CO_2H \rightleftharpoons -CO_2^- + H^+$	4.4
His side-chain		6.5
Terminal amino	$-NH_3^+ \rightleftharpoons -NH_2 + H^+$	8.0
Cys side-chain	$-SH \rightleftharpoons -S^- + H^+$	8.5

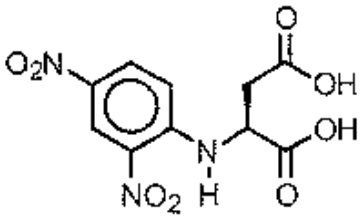
Table 2 (continued)

Tyr side-chain		10.0
Lys side-chain amino	$-NH_3^+ \rightleftharpoons -NH_2 + H^+$	10.0
Arg side-chain	$-NH(NH_2)C=NH_2^+ \rightleftharpoons -NH(NH_2)C=NH + H^+$	12.0

SOLUTION

6.1 Two sulphonic acid groups are formed from oxidation of a disulfide bond.

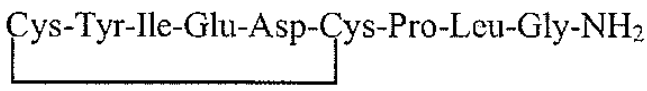
6.2 Complete structure of DNP-Asp at its isoelectric point is



6.3 The sequence of B8 is: Cya-Tyr-Ile-Glu

6.4 The sequence of B9 is: Asp-Cya-Pro-Leu

6.5 The *complete* structure of A is



6.6 Write the revised structure of A below and circle the site(s) to indicate all the possible source of ammonia

6.7 The isoelectric point of A is 9.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

A Kinetic Study of the Acid Catalyzed Reaction Between Acetone and Iodine in Aqueous Solution

The reaction between acetone and iodine in aqueous solution is catalyzed by H^+.

$$CH_3\text{-}CO\text{-}CH_3\ (aq) + I_2\ (aq) \xrightarrow{H^+} CH_3\text{-}CO\text{-}CH_2I\ (aq) + H^+(aq) + I^-(aq)$$

In this experiment, the kinetics of the iodination is measured to determine the rate law of the reaction. The rate equation for the loss of I_2(aq) has been shown to have the form

$$\text{Rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

where H^+ ions are the catalyst.

In order to determine the rate constant k and the kinetic orders x, y and z, the initial rate of reaction is measured.

$$\text{Initial rate} = k\,[CH_3COCH_3]_0^x\,[I_2]_0^y\,[H^+]_0^z$$

where $[\ ]_0$ are the initial concentrations of acetone, I_2 and H^+, respectively.

If the initial rates are measured for various initial concentrations of the reactants then the order with respect to each reactant can be obtained.

The initial rate is obtained by measuring the decrease in the I_2(aq) concentration after a short time interval (7.0 min. in this experiment) after the start of the reaction. Aqueous sodium acetate solution is added to stop the reaction after 7 minutes. The acetate ion reacts immediately with the H^+ to produce acetic acid and so reducing the concentration of H^+. The reaction is thus stopped as there is no catalyst present.

Since the reaction does not come to a complete halt, the solution should be titrated immediately after the addition of the sodium acetate solution.

The remaining iodine I_2 (aq) is determined by titration with sodium thiosulphate, $Na_2S_2O_3$. As the end point of the titration is approached, starch indicator is added and the titration is continued until the blue colour disappears.

Chemicals

1. Aqueous iodine solution in 0.4 M KI 80 cm^3
2. 0.100 M aq. HCl 50 cm^3
3. 0.50 M aq. CH_3COONa 80 cm^3
4. Standard 0.02 M $Na_2S_2O_3$(aq) solution 200 cm^3
   (the exact concentration will be announced at the beginning of practical part)
5. Aqueous acetone (50% by volume) 50 cm^3
   (Density of pure acetone; 0.787 g cm^{-3}, MW. = 58.08)
6. Starch indicator 7 cm^3

Procedure

A. Standardization of Iodine Solution

1. Pipet 5.00 cm^3 of aqueous iodine into a clean 125 cm^3 Erlenmeyer flask.
2. Add 10 cm^3 of distilled water using graduated cylinder.
3. Titrate the iodine with the standard 0.02 M sodium thiosulphate solution until the colour of the solution is pale yellow.
4. Add 3 – 4 drops of starch indicator and continue the titration until the blue colour disappears.
5. Record the initial and the final volumes of the thiosulphate solution and the volume used in the answer sheet.
6. Repeat the titration as necessary (Steps 1 to 5).
7. Give the titre volume for calculation in the answer sheet.
8. Calculate the iodine concentration.

B. A kinetic study of acid catalyzed reaction between acetone and iodine in aqueous solution

1. Label the stoppered flasks as follows: Flask I, II, III and IV.
2. To each respective flask add the following volumes of distilled water, 0.100 M hydrochloric acid and 50 % acetone:

Flask No.	Volume (cm^3)		
	water	0.100 M HCl	50 % acetone
I	5.00	5.00	5.00
II	0.0	5.00	5.00
III	0.0	5.00	10.00
IV	0.0	10.00	5.00

Stopper each flask immediately after addition of the solutions.

3. Measure out 10 cm^3 of 0.50 M aq. CH_3COONa into the graduated cylinder.
4. Set the stop-watch to 0.0000 display.
5. Pipet 5.00 cm^3 of iodine solution into the stoppered Flask No. I.
   Start the stop-watch as soon as the first drop of iodine solution is added.
6. Stopper the flask and swirl continuously.
7. Just before 7.0 min, remove the stopper, at 7.0 min, immediately pour 10 cm^3 of sodium acetate solution (from step 3) into the reaction flask. Shake well.
8. Titrate the remaining iodine with standard thiosulphate solution.
9. Record the volume of the thiosulphate solution.
10. Repeat the above steps (Steps 3 to 9) for Flask II, III and IV but add in step 5 the I_2(aq) solution to each flask as indicated:

    Flask II: 10.00 cm^3 I_2 solution
    Flask III: 5.00 cm^3 I_2 solution
    Flask IV: 5.00 cm^3 I_2 solution

Calculations

B-1. Calculate the initial concentrations (M) of iodine, acetone and HCl solutions in Flasks I to IV, assuming volumes are additive.

B-2. Calculate concentrations of iodine (M) remaining in Flasks I to IV at 7.0 minutes.

B-3. Calculate the initial reaction rate for Flasks I to IV in M s^{-1}.

B-4. The rate of reaction has the form

$$\text{Rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

Calculate the reaction orders x, y and z from the initial rates and the initial concentrations of acetone, iodine and HCl. The values of x, y and z should be rounded off to the nearest integer and fill in the answer sheet. Write rate equation or rate law.

B-5. Calculate the rate constant, k, for Flasks I to IV with proper unit.

B-6. Give the mean value of the rate constant.

SOLUTION

The competitors were required to perform the following tasks:

In part A: Using the concentration of standard $Na_2S_2O_3$ solution (in bottle) and titration results it was required to calculate the concentration of iodine in the solution. Results were expected to be shown in a table in the answer sheet.

In part B: The following calculations B1 – B5 were required to be shown in the answer sheet:

B-1. *Calculation for initial concentrations (M) in the solution mixtures.*

B-2. *Calculation of the concentration (M) of iodine remaining in flasks I to IV at 7 minutes.*

B-3. *Calculation of initial rate of disappearance of I_2 at 7 minutes in flasks I to IV*.

$$\text{Rate of disappearance of iodine (M s}^{-1}) = -\frac{d[I_2]}{dt} = \frac{c(I_2)_{\text{initial}} - c(I_2)_{7\,\text{min}}}{7 \times 60\ s}$$

B-4. *Calculation of x, y, and z in the rate equation*:

$$\text{rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

In comparing the rates in solutions **II** : **I**, **III** : **I**, and **IV** : **I** one can calculate the following values:

x = 1; y = 0; z = 1

The rate equation has the form: rate = $k\,[CH_3COCH_3]\,[H^+]$

B-5. *Calculation of the rate constants for solution mixtures **I** to **IV** and the mean value of the rate constant.*

PROBLEM 2 (Practical)

Isolation and Identification of an Essential Oil from Natural Source

In this experiment, you will steam distil and determine the structures of the main essential oil (**S**) from a given natural source and a product from its chemical conversion (unknown **Y**).

To determine the structures, you have to use organic qualitative analysis to identify any functional groups present in the compounds by using the reagents at your station. NMR data will be given only after the functional group test is completed.

Chemicals Available:

Sample (1 g in a vial)

Unknown **Y** (in a vial)

Anhydrous Na_2SO_4 (in a plastic vial), dichloromethane, ceric ammonium nitrate solution, 2,4-Dinitrophenylhydrazine (labelled as 2,4-DNP), 2 % aq. NH_3, 5 % aq. $AgNO_3$, 5 % aq. HCl, 5 % aq. NaOH, 5 % aq. $NaHCO_3$, 1 % $FeCl_3$ in EtOH, 0.2 % aq. $KMnO_4$, decolourised with easily oxidised functional groups, acetone (for washing).

Procedure:

1. Apparatus: Assemble a distillation apparatus using a 25 cm^3 round bottomed flask for distillation and a 10 cm^3 round bottomed flask to collect the distillate. Heat the sand bath to approximately 150 °C before proceeding the next step.

Simplified Steam Distillation: Mix 1 g of ground sample with 15 cm^3 of water in the 25 cm^3 round bottomed flask and allow the sample to soak in the water for about 10 minutes before distillation. Do not forget to put in a magnetic bar, turn on the water in the condenser and stirring motor, heat the mixture (the temperature of the sand bath should not be below 170 °C) to provide a steady rate of distillation. At least 5 cm^3 of distillate must be collected. Hot plate must be turned off after distillation is finished. Disassemble the apparatus and rinse the condenser with acetone. Be sure that the condenser is dry before using in the next step

Extraction of the Essential Oil: Transfer the distillate to a 15 cm^3 capped centrifuge tube and add 1 cm^3 of dichloromethane to extract the distillate. Cap the tube securely and shake vigorously, cool in ice. Allow the layers to separate.

Using a Pasteur pipette, transfer the dichloromethane layer to a 10 cm^3 test tube. Repeat this extraction with fresh 1 cm^3 dichloromethane twice and combine with the first extract.

Drying: Dry the dichloromethane extract by adding anhydrous Na_2SO_4 and stir occasionally for 10 minutes.

Evaporation: With a clean, dry cotton plugged Pasteur pipette transfer the organic layer to a dry 5 cm^3 conical vial. Use approximately 1 cm^3 of clean dichloromethane to wash Na_2SO_4 using the dry cotton plugged Pasteur pipette, then transfer into the vial. Be careful not to transfer any of the Na_2SO_4 into the vial. Use Hickman still head and dry condenser to distil the dichloromethane from the solution until the volume is reduced to 1 cm^3. Discard the distilled dichloromethane from the Hickman still head with a Pasteur pipette or a syringe to a vial (for recovered dichloromethane) and keep the residue for functional group analysis.

Functional Group Analysis: Carry out the functional group analysis of the residue solution (1 cm^3) by using the appropriate reagents at your station. (Note: dichloromethane is immiscible with water.)

Tollen's Reagent: add 1 drop of 5 % aq. $AgNO_3$ in a small test tube followed by 1 drop of 5 % aq. NaOH, brown precipitate will appear. Add 2 % aq NH_3 to the tube until all the precipitate dissolved. The solution is ready for the test.

2. Structure elucidation of the main essential oil (S)

Reaction of the main essential oil (**S**) with CH_3I in the presence of K_2CO_3 gives compound **X** ($C_{11}H_{14}O_2$). Oxidation of **X** gives unknown **Y** ($C_{10}H_{12}O_4$) as the main product and CO_2.

3. Structure elucidation of the unknown Y:

Identify the functional groups of unknown Y (provided in a conical vial) by using the reagents at your station and fill in your results in the answer sheet. Indicate the functional group(s) present or not present.

Hand in your copy of answer sheet PART I (Demonstrator copy) of functional group analysis and ask for ^{1}H NMR spectra. ^{1}H NMR spectra will be given only when the functional group analysis is completed.

4. Draw the structure which represents the main component in the essential oil (S) that was distilled from the sample. Assign each proton from the provided ^{1}H NMR spectra by labelling the peak number on the proton in the structure in the answer sheet.

5. Draw the structures of compound X and unknown Y. Assign each proton of unknown **Y** from the provided ^{1}H NMR spectra in the same manner as in (4).

SOLUTION

1. It was expected to obtain at least 5 cm^3 of distillate.

2. Functional group analysis of the distilled essential oil:

Reagents	Positive test	Negative test
0.2 % $KMnO_4$	✓	
1 % $FeCl_3$	✓	
2,4-DNP		✓
Ceric ammonium nitrate	✓	
Tollen's Reagent		✓

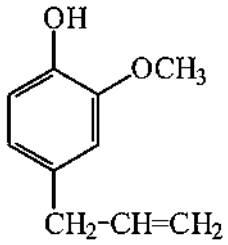
Functional groups in S	Present	Not present
-C=C-	✓	
-OH (alcoholic)		✓
-OH (phenolic)	✓	
-CHO		✓
-CO-		✓
-COOH		✓

3. Funcional group analysis of the unknown compound Y:

Reagents	Positive test	Negative test
5 % HCl		✓
5 % NaOH	✓	
5 % $NaHCO_3$	✓	
0.2 % $KMnO_4$		✓
1 % $FeCl_3$		✓
2,4-DNP		✓
Ceric ammonium nitrate		✓
Tollen's Reagent		✓

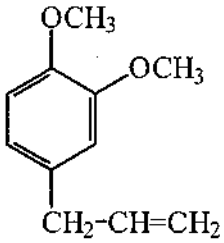
Functional groups in **Unknown Y**	Present	Not present
-C=C-		✓
-OH (alcoholic)		✓
-OH (phenolic)		✓
-CHO		✓
-CO-		✓
-COOH	✓	

4. The structure which represents the main essential oil (S):

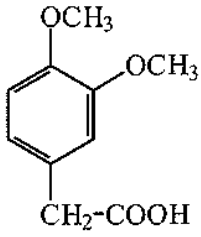


5. The structure of compound **X** and unknown **Y**:

Compound **X**



Compound **Y**

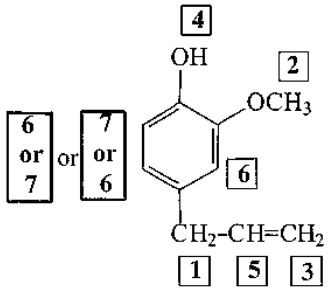


NMR spectrum of the main essential oil (S):

(See peak number in the given 'H NMR spectrum)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity
1	3.31	2H	d
2	3.84	3H	S
3 4	5.0 – 5.1	2H	m
5	5.6	1H	S
	5.9 – 6.0	1H	m
6	6.7	2H	S d or m
7	6.87	1H	d

NMR assignment of the main essential oil (S):



NMR spectrum of the unknown **Y**:

(See peak number in the given 'H NMR spectrum. Labile proton does not appear in the spectrum.)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity
1	3.59	2H	s
2	3.86	3H	s
3	3.88	3H	s
4	6.81	3H	s

NMR assignment of the main essential oil (S):